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COMPLETE SPECIFICATION

CADMIUM-FREE BRAZING ALLOYS

We, **DEGUSSA-HÜLS AKTIENGESELLSCHAFT, a German company of D-60287 Frankfurt am Main, Federal Republic of Germany** hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:

PT05A14192

(followed by page 1a)

Cadmium-free brazing alloys

The invention relates to cadmium-free, low-melting brazing alloys having good wetting ability on hard metals.

Soldering is an economical method of joining which is particularly mild on materials and is of great technical importance both in series production and in the joining of individual parts. A great advantage of soldering is that materials can be bonded to one another by the solder alone at relatively low temperatures. The lower the soldering temperature, the smaller are the energy consumption, the influence of the structure of the parent materials and, in general, the soldering defects as well. Low-melting brazing solders are therefore particularly in demand.

In addition to Ag, conventional silver-based solders contain Cu, Zn, Sn, In as the main alloying elements and optionally other elements. Silver solders which contain cadmium are low-melting, easy to solder and versatile. However, cadmium and in particular its vapours are carcinogenic. For this reason, such solders are permitted to be used only if strict safety precautions are complied with. The advantage of the cadmium-containing solders is their particularly low melting range and the particularly low soldering temperatures which are consequently possible. These have not been achieved by the conventional cadmium-free Ag-based solders until recently.

However, Ag brazing solders which, even without the addition of cadmium, achieve soldering temperatures of below 630°C have also been known for several years. In essence, this is achieved because these soldering alloys contain the element Ga in a differentially matched ratio to the other alloying elements.

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Alloys of this type are described, for example, in the patent specifications DE 43 15 190, DE 43 15 189, DE 43 15 190 and DE 43 23 227. These alloys are specifically conceived as a substitute for the low-melting cadmium-containing solders.

Low soldering temperatures are desirable particularly in the soldering of hard metals, in order that the thermally induced cooling stresses arising as a result of the different coefficients of thermal expansion of the hard metal and of the support material can be kept as low as possible. In addition to the difference between the coefficients of expansion, namely the temperature difference between solidification temperature of the solder and room temperature is decisive in determining the magnitude of the induced stresses. In the machine tools industry, and especially for use in drilling heads, diamond-coated hard metals having a particularly high resistance to abrasion are used. For technical reasons it is necessary that these diamond-coated hard metals be soldered to the support materials in air with the use of fluxes, so the soldering temperature must under no circumstances exceed ca. 690°, so as not to damage the diamond layer. The lower the soldering temperature, the higher in this case is the reliability of the process and of the product quality.

It has been found, however, that the gallium-containing solders known from the above-mentioned documents do not adequately wet hard metals, in fact especially the hard metals used as drilling heads, so that the soldering process is thereby impeded.

Accordingly, the object of the invention was to develop brazing solders having soldering temperatures of below 650°C, which are free from toxic constituents such as, in particular, cadmium and which moreover exhibit a very good

wettability of hard metals, or to at least provide a useful alternative. In addition, these solders are to be particularly suitable for soldering diamond-coated hard metals.

This object is achieved according to the invention by cadmium-free brazing alloys, which are characterised in that they contain 45-75 wt.% Ag, 10-30 wt.% Cu, up to 20 wt.% Ga, 1-25 wt.% Zn, up to 6 wt.% Sn or In or up to 6 wt.% Sn and In, 0.1-8 wt.% Mn and/or 0.1-3 wt.% Si or Ge or 0.1-3 wt.% Si and Ge and optionally up to a total of 5 wt.% of other alloying elements.

The cadmium-free brazing alloys according to the invention may contain preferably up to 5 wt.% of the other alloying elements Co or Ni.

Alloys of the following composition have proved to be very successful:

50 - 70 wt.% Ag

10 - 20 wt.% Cu

1 - 20 wt.% Ga

5 - 20 wt.% Zn

0 - 6 wt.% Sn or In or Sn and In

0.1 - 8 wt.% Mn or

0.1 - 2 wt.% Si or Ge or Si and Ge.

Alloys of the following composition are particularly preferred:

50 - 60 wt.% Ag

10 - 20 wt.% Cu

1 - 10 wt.% Ga

Owing to the comparatively small proportion of Mn as alloying component, the solders according to the invention can be very easily cast and formed and hence can be worked and processed without difficulty in the production process.

A particularly surprising and unexpected property of the brazing solders according to the invention is their excellent wetting behaviour on hard metals.

To assess the wetting ability of the solders on hard metal, round pieces of solder of defined thickness (0.2 mm) and size (5 mm ø), which have been punched out from various soldering alloys, are placed onto hard metal samples, flux is applied and these samples are brought to soldering temperature in an oven in air at a heating rate typically applied in practice. After the samples have been cooled, the surface area of the hard metal wetted with solder is determined and the ratio of the initial surface area of the pieces of solder is found. The result is shown in Table 1 under the column headed "wetting index". Surprisingly, it is apparent that the solders according to the invention have a considerably better wetting ability on hard metal than do the known cadmium-free, gallium-containing brazing solders.

Another advantage, relevant in practice, of the brazing solders according to the invention is the increase in the shear strength of the soldered joints thus produced.

By virtue of the properties presented above, the cadmium-free brazing alloys according to the invention are particularly suitable for soldering hard metals, such as in particular in the soldering of diamond-filled or diamond-coated hard metal segments, for instance, in the production of drilling heads.

Table 1

No.	Ag	Cu	Ga	Zn	Sn/In	Mn/ Si/Ge	Operating temper- ature °C	Wetting index (1)
1	56	18.5	3	17	5(Sn)	0.5 (Mn)	620	3
2	56	16	3	17	3 Sn 2 In	3(Mn)	610	5
3	56	14	3	17	5(Sn)	5(Mn)	635	7
4	62	15	15	7	-	1(Si)	600	4
5	62	13	15	7	-	1 Si 2 Ge	580	5
6	62	11	15	7	-	5(Mn)	615	6
7	54	20	3	17	5(Sn)	1(Ge)	610	3.5
8	55	20	3	17	5(Sn)	-	630	1.5
9	63	15	15	7	-	-	600	2

(1) Wetting index: = Ratio of initial surface area / soldered surface area.

What We Claim Is:

1. Cadium-free brazing alloy including:
45-75 wt.% Ag, 10-30 wt.% Cu, up to 20 wt.% Ga, 1-25 wt.% Zn, up to 6 wt.% Sn or In or up to 6 wt.% Sn and In, 0.1-8 wt.% Mn or 0.1-3 wt.% Si or Ge or Si and Ge and optionally up to a total of 5 wt.% of other alloying elements provided that when Ga is 12 wt.% or less, either Mn and/or Si is present.

2. Brazing alloy according to claim 1, including up to 5 wt.% of the other alloying elements Co or Ni.

3. Brazing alloy according to claim 1 or 2, including:

50 - 70 wt.% Ag

10 - 20 wt.% Cu

1 - 20 wt.% Ga

5 - 20 wt.% Zn

0 - 6 wt.% Sn or In or Sn and In

0.1 - 8 wt.% Mn or

0.1 - 3 wt.% Si or Ge or Si and Ge.

4. Brazing alloys according to any one of claims 1 to 3, including:

50 - 60 wt.% Ag

10 - 20 wt.% Cu

1 - 20 wt.% Ga

10 - 20 wt.% Zn

1 - 6 wt.% Sn or In or Sn and In

0.1 - 8 wt.% Mn

5. Brazing alloys according to any one of claims 1 to 3, including:

60 - 70 wt.% Ag

10 - 20 wt.% Cu

10 - 20 wt.% Ga

5 - 10 wt.% Zn

0.1 - 8 wt.% Mn or

0.1 - 3 wt.% Si or Ge or Si and Ge.

6. Use of the brazing alloys with a high silver content according to claims 1 to 5 for soldering hard metals.

7. Use according to claim 6 for soldering diamond-filled or diamond-coated hard metal segments in the production of drilling heads.

8 A cadmium-free brazing alloy according to claim 1 substantially as herein described with reference to the compositions numbered 1 to 7 in Table 1.

9. A cadmium-free brazing alloy according to any one of claims 1 to 5 substantially as herein described with reference to the compositions numbered 1 to 7 in Table 1.

10. A cadmium-free brazing alloy according to any one of claims 1 to 5 substantially as herein described.

11. The use of a brazing alloy according to claim 6 or claim 7 substantially as herein described with reference to the compositions numbered 1 to 7 in Table 1

12. The use according to claim 6 or claim 7 substantially as herein described.

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Cadmium-free brazing alloys

Abstract:

The invention relates to cadmium-free brazing alloys which are characterised in that they contain 45-75 wt.% Ag, 10-30 wt.% Cu, up to 20 wt.% Ga, 1-25 wt.% Zn, up to 6 wt.% Sn and/or In, 0.1-8 wt.% Mn or 0.1-3 wt.% Si and/or Ge and optionally up to a total of 5 wt.% of other alloying elements.

Owing to their low operating temperatures and their excellent wetting ability, these solders are particularly suitable for soldering hard metals.